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AGENTS IN PLANTS

(57) Abstract

Methods and compositions are provided for enhancing uptake of a plant active agent, particularly herbicides, which have structures capable of equilibrating to acidic and basic species in the presence of water. The bioactive agent is mixed with an uptake and transport-enhancing adjuvant comprising an anionic surfactant and a mixture of water-immiscible, low-vapor pressure, vegetable-derived oils.

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METHOD AND COMPOSITION FOR ENHANCING UPTAKE
AND TRANSPORT OF BIOACTIVE AGENTS IN PLANTS

The present invention is directed to a method and composition for enhancing uptake and transport of
5 bioactive agents, such as herbicides, insecticides, fungicides, plant growth regulators, fertilizers, and the like, in plants.

BACKGROUND OF THE INVENTION

Many bioactive chemicals, and in particular herbicides,
10 have been developed which are either highly selective to particular plant species, climate sensitive or are in some instances very expensive to use. Also, it is recognized that only a portion of an applied bioactive agent, such as a herbicide, is actually biologically
15 engaged in the plant. Thus more efficient utilization of the applied bioactive agent is required. It has been surprisingly found that uptake and transport of plant active agents, particularly herbicides, where the bioactive agent has a molecular structure capable of
20 equilibrating in presence of water to acidic and basic species, can be enhanced by use in conjunction with an adjuvant comprising anionic surfactants and low-vapor-pressure, water-immiscible liquids.

It is an object of the present invention, therefore, to
25 provide a plant active composition comprising a bioactive agent and adjuvant which provides more effective use of

the bioactive agent by enhancing uptake and transport into the plant.

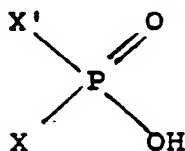
Another object of the present invention is to increase the efficacy of herbicides and other plant-active agents.

- 5 These and other objects will be apparent from the following description, disclosure and by practice of the invention.

SUMMARY OF THE INVENTION

- A method and composition are provided for enhancing uptake of bioactive agents in plants whereby a composition is applied to the plant having the following components: a bioactive agent having a molecular structure capable of equilibrating to acidic and basic species in water and an uptake-enhancing adjuvant. The adjuvant comprises 20-60% (w/w) of an anionic surfactant; 40-60% (w/w) of fatty acids, fatty acid esters or mixtures thereof; and 10-40% (w/w) of polyalkylene glycol esters of fatty acids. A preferred class of anionic surfactants comprises phosphate esters of the formula

20



25 X is HO- or $\text{-(O(CH}_2\text{)}_m\text{)}_n\text{-OR}'$;

X' is $\text{-(O(CH}_2\text{)}_m\text{)}_n\text{-OR}'$;

- wherein R' is an alkyl or alkaryl group containing 5-50 carbon atoms; m is 2 or 3; and n is an integer from 1 to about 50. The most preferred class of anionic surfactants are those in which m=2, n is from 2 to 9; R' is C₁₁-C₁₄ (if R' is alkyl) or R' is C₁₅-C₃₀ (if R' is

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alkaryl). If R' is alkaryl, nonylphenyl and dinonylphenyl groups are preferred.

Another class of anionic surfactants comprises those of the formula R^5-SO_3H wherein R^5 is linear or branched alkyl or alkenyl containing 6 to about 50 carbon atoms, or R^5 is



wherein R^6 is alkyl or alkenyl containing 1 to about 30 carbon atoms.

The adjuvant also comprises about 40-60% (w/w) of fatty acids, fatty acid esters or mixtures thereof. Lower alkyl esters are preferred.

The adjuvant also comprises 10-40% (w/w) of polyalkyleneglycol esters of fatty acids. Polyethylene glycol esters are particularly preferred, most preferably where the polyethylene glycol moiety has an average molecular weight in the range of about 200 to 1000.

Optionally, the adjuvant may contain 10-40% (w/w) of other components which are well known in the art as quality enhancement agents. These include antioxidants, emulsifiers, film formers and diluents.

DISCLOSURE OF THE PREFERRED EMBODIMENTS

The bioactive agent used in conjunction with the present invention may be any bioactive agent such as a herbicide, insecticide, fungicide, plant growth regulator, fertilizer, and the like, which has a molecular structure capable of equilibrating in an aqueous system to acidic and basic equilibrium species. These acidic and basic species are interconvertible by addition or removal of

protons. For example, in the following generic representation of the equilibrium process, HA and A⁻ are in the acidic and basic forms of the bioactive agent:

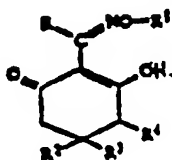


- 5 Particularly preferred bioactive agents are herbicides which are disclosed in Patent No. 4,440,566.

The adjuvant according to the present invention will comprise an anionic surfactant (which is acidic in water), and other low-vapor-pressure (less than 3 mm/Hg.
10 at 20°C), water immiscible-liquids, selected from the group which includes fatty acids, fatty-acid esters, and mixtures thereof, as described below.

- Preferably all of these components will have a vapor pressure of less than 1 mm (at atmospheric pressure).
15 It is a particular advantage of the adjuvant that the components have low volatility, which minimizes environmental pollution. Furthermore, the vegetable derived materials which are used (fatty acids and esters) are non-toxic and degrade rapidly in the environment.
20 These are significant advantages over many adjuvants of the current art which contain hydrocarbons.

A preferred class of bioactive agents are herbicides of the structure



wherein

- 25 R is alkyl of 1 to 6 carbon atoms or phenyl;
R' is haloalkenyl of 2 to 6 carbon atoms and 1 to 3
halogen atoms, p-halobenzyl or p-trifluoromethylbenzyl;

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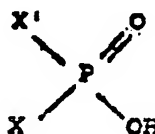
R^2 and R^3 are independently hydrogen, alkyl of 1 to 3 carbon atoms, alkylthio of 1 to 6 carbon atoms, or alkylthioalkyl of 2 to 8 carbon atoms;

R^4 is hydrogen or carbalkoxy of 2 to 4 carbon atoms.

- 5 Particularly, the preferred compounds are those wherein R^4 is hydrogen, and R is alkyl of 1 to 6 carbon atoms, and R^1 is haloalkenyl. Other preferred compounds are those wherein R is ethyl or propyl, and one of R^2 or R^3 is hydrogen and the other is alkylthioalkyl. Many of
- 10 the preferred compounds are those in which R is ethyl or propyl and one of R^2 or R^3 is hydrogen and the other is 2-ethylthiopropyl and R^1 is haloalkenyl. The group R^4 may also be 3-trans-chloroallyl.

The anionic surfactants will be those with an acid

15 dissociation constant (pKa) in the range of about 0.1 to 5.0, preferably from 1 to 5. A preferred class of anionic surfactants are alkoxylated phosphoric acid esters of the following formula



X is HO- or $(O-CH_2)_m-$ OR';

X' is $(O-CH_2)_n-$ OR';

wherein R' is an alkyl group or alkaryl group containing

20 5-50 carbon atoms; m is 2 or 3; and n is an integer from 1 to 50.

Alkyl and alkaryl groups include, but are not limited to, decyl, lauryl, tridecyl, oleyl, stearyl, nonylphenyl, octylphenyl, dinonylphenyl, dioctylphenyl, d-decylphenyl,

25 octylnaphthyl, dioctylnaphthyl, and the like.

Preferably $m=2$, n is from 2 to 9 and R' is C_{11} - C_{14} alkyl or C_{15} - C_{30} alkaryl. The lauryl, tridecyl, nonylphenyl, and dinonylphenyl groups are preferred.

Another class of surfactants includes sulfonic acids of formulas R^5-SO_3H wherein R^5 is linear or branched C_6 to C_{50} , alkyl or alkenyl or R^5 is



and R^6 is C_1 - C_{30} alkyl, preferably linear C_8 - C_9 . R^5 is preferably C_{12} - C_{30} alkyl or alkenyl.

Particularly preferred anionic surfactants for use in the adjuvant are those in which X is OH or $(O(CH_2)_m)_nOR'$. Particularly preferred anionic surfactants are those in which m is 2, n is 2 to 9, and most preferred R' is decyl, lauryl, tridecyl, or dialkylphenyl. The most preferred anionic surfactants are those in which R' is tridecyl or dinonylphenyl.

The low vapor-pressure, water-immiscible liquids which are particularly preferred are fatty acids and their ester derivatives. The adjuvant will comprise 40-60% (w/w) fatty acids or fatty acid esters, such as isostearic acid, methyl oleate and the like. Also, the adjuvant will contain from 10-40% (w/w) of a polyalkylene glycol ester of fatty acids. The polyalkylene glycol moiety which is particularly preferred in polyethylene glycol, typically having an average molecular weight in the range of 200 to 1000, with 400 being most preferred.

In a most particularly preferred composition, a cyclohexane dione herbicide concentrate (2 lb./gallon containing an emulsifier and a solvent) is used by combining a sufficient amount of such a concentrate to provide 0.1 lbs. (active basis) of the herbicide, with

- 20 gallons of water. A second composition, an adjuvant mixture, is made comprising 70% of fatty acid esters and 30% of the mixture comprising a phosphoric ester surfactant wherein $X=OH$, $m=2$, $n=3$ and R' =tridecyl. The
- 5 adjuvant mixture and the water mixture containing the herbicide are then mixed wherein the adjuvant weight to aqueous herbicidal mixture weight ratio is between about 1:5 and 1:1000, respectively. A particularly preferred ratio is between 1:200 and 1:300.
- 10 It is particularly advantageous in that while the cyclohexane dione herbicides, particularly those useful against grassy weeds, are normally applied at a rate of from 30 to 567 g/ha, according to the present invention they are equally efficacious when applied at about 40%
- 15 or less of that rate with the uptake-enhancing agent.

Suitable bioactive agents which may be utilized in connection with the present invention include, but not limited to, compounds such as

Herbicides

- 20 clethodim (SELECT)
- 4-chloro-2-oxo-3(2H)-benzothiazoleacetic acid
(benazolin)
- 3-(1-methylethyl)-1(H)-2,1,3-benzothiadiazin-4(3H)-
one 2,2-dioxide (bentazone, BASAGRAN)
- 25 3,5-dibromo-4-hydroxybenzonitrile (bromoxynil)
- 3-amino-2,5-dichlorobenzoic acid (chloramben,
AMIBEN)
- 3,6-dichloro-2-pyridinecarboxylic acid (clopyralid,
LONTREL)
- 30 2-[1-(ethoxyimino)butyl]-3-hydroxy-5-(tetrahydro-
2H-thiopyran-3-yl)-2-cyclohexene-1-one (cycloxydim)
- (2,4-dichlorophenoxy)acetic acid (2,4-D)

- 3,6-dichloro-2-methoxybenzoic acid (dicamba, BANVEL)
- N-(phosphonomethyl)glycine (glyphosate)
- 5 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid (imazaquin, SCEPTER)
- 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid (picloram, TORDON)
- 10 2-[1-(ethoxymino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one (sethoxydim, POAST)
- 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid (acifluorfen, BLAZER)

Fungicides

- 2,2'-methylenebis(4-chlorophenol) (dichlorophen)
- 15 5-butyl-2-(dimethylamino)-6-methyl-4(1H)-pyrimidinone (dimethirimol)

Insecticides

- O,S-dimethyl acetylphosphoramidothioate (ORTHENE)
- 20 cyano(3-phenoxyphenyl)methyl 4-chloro(1-methylethyl)benzene acetate (fenvalerate, PYDRIN)

PGR

- 2-(3-chlorophenoxy)propanoic acid (3-CPA, FRUITONE CPA)
- (2-chloroethyl)phosphonic acid (ethephon)
- 25 1H-indole-3-acetic acid
- 1-naphthaleneacetic

The compositions according to the present invention are beneficially employed to promote uptake and transport of systemic herbicides, fungicides, pesticides, plant growth regulators, fertilizers and the like. It is to be understood that combinations of the above bioactive

30

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agents can be employed, as in available commercial formulations, and are generally applied at rates recommended by the supplier of the bioactive agent. However, increased benefits with herbicides or other
5 bioactive agents having the requisite proton exchange ability can be realized when the bioactive enhancing agent is utilized therewith.

A particularly preferred utilization is that with a herbicide as disclosed in Patent No. 4,440,566 which is
10 incorporated by reference herein in its entirety. As such, the herbicides may be used primarily as a post-emergent herbicide. The amount of active herbicidal compound administered will vary with the particular plant or plant growth medium which is to be contacted, the
15 general location of an application, i.e., sheltered areas such as greenhouses, as compared to exposed areas such as fields, as well as desired type of control. Generally, for illustrative purposes, under greenhouse conditions, for post-emergent herbicidal control, SELECT,
20 a herbicidal compound having a cyclohexane dione moiety would normally be applied at a rate of about 28 g/ha. However, when used in conjunction with the bioactive enhancing agent the equivalent activity may be obtained within an application rate at 5 g/ha or less, with no
25 damage to broadleaf crops (see Tables 1 through 5). Similar relative enhancement under field conditions is obtained (see Table 6). Normal field application rates of SELECT are about 30-120 g/ha (for control of annual grasses, and usually about 120-567 g/ha for control of
30 established perennial species. Addition of 0.1-1% (v/v) (preferably 0.3-0.5% (v/v)) of the bioactive-enhancing agent to the aqueous spray solution of the herbicide enhances the activity and reduces the necessary rate of application of the herbicide.

The adjuvant may contain optional emulsifiers, dispersants, binders, stabilizers and the like, which are well known in the art as functional additives that optimize formulations.

5 Post-Emergent Herbicidal Test

The bio-active agent and adjuvant were homogeneously dispersed in water and sprayed on the plants. The compositions of the spray mixtures are indicated in the Tables 1-6. Each formulation was uniformly sprayed on
10 plants. Greenhouse plants were 2 to 4" tall (approximately 5 to 25 plants per pot) at treatment. After the plants were sprayed and allowed to dry, they were placed in a greenhouse and then watered intermittently at their bases, as needed. The plants
15 were observed periodically for phytotoxic effects and physiological and morphological responses to the treatment. After 3 weeks, the herbicidal effectiveness of the compound was rated based on these observations. A 0-to-100 scale was used, 0 representing no
20 phytotoxicity and 100 representing complete kill. The application rates of Select were as % active ingredient. The results of these tests appear in the Tables 1-5.

The following examples are provided to assist in the understanding of the invention and are not to be
25 construed as limiting the scope of the invention. In the following attached Tables 1-6 the herbicidally active compound (a herbicide disclosed in Patent No. 4,440,566) known as Clethodim is used. It is usually sold as a formulation known as Select.

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TABLE 1

Percent Phytotoxicity of Select With and Without
Adjuvant on Grass and Broadleaf Plants
Greenhouse Test

5

	Weeds and Crop Plants	Select* 0 gr/ha Adjuvant 0.25%v/v	Select 28 gr/ha Adjuvant 0%v/v	Select 11 gr/ha Adjuvant 0.25%v/v	Select 11 gr/ha Adjuvant 0.125%v/v
10	Blackgrass	0	91	90	88
	Wild Oats	0	56	81	68
	Cheatgrass	0	46	85	63
	Crabgrass	0	43	76	71
	Barnyard Grass	0	91	86	80
15	Goosegrass	0	90	90	80
	Sprangletop	0	94	91	93
	Italian Ryegrass	0	81	90	88
	Fall panicum	0	91	91	91
20	Proso millet	0	88	90	90
	Yellow foxtail	0	86	85	85
	Johnsongrass	0	71	86	85
	Rice	0	50	56	50
	Sorghum	0	81	76	73
25	Wheat	0	40	46	26
	Field corn	0	63	63	63
	MEAN GRASSES	0	73	80	75
30	Sugarbeets	0	0	0	0
	Canola	1	1	3	1
	Soybean	1	1	1	3
	Cotton	6	3	0	0
35	MEAN BROADLEAF CR	2	1	1	1
	*Application rates of SELECT are given as active ingredient. The Adjuvant is 30% (wt.) alkylphosphoric acid ester (R' = tridecyl, m = 2, n = 3) 20% (wt.) PEG 400 dioleate, and 50% (wt.) methyl oleate (EMEREST 2301). The compositions are spray emulsions of the				

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formulated active ingredient, adjuvant and water. Addition of
adjuvant significantly improved the activity of Select.

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TABLE 2

Percent Phytotoxicity of Select With and Without
Adjuvant on Grass and Broadleaf Plants
Greenhouse Test

5

Weeds and Crop Plants	Select 0 gr/ha Adjuvant 0.25%v/v	Select 11 gr/ha Adjuvant 0%v/v	Select 11 gr/ha Adjuvant 0.25%v/v	Select 11 gr/ha Adjuvant 0.125%v/v
Blackgrass	0	43	90	88
Wild Oats	0	0	81	68
10 Cheatgrass	0	0	85	63
Crabgrass	0	10	76	71
Barnyard Grass	0	50	86	80
Goosegrass	0	10	90	80
15 Sprangletop	0	3	91	93
Italian Ryegrass	0	0	90	88
Fall panicum	0	68	91	91
Proso millet	0	43	90	90
20 Yellow foxtail	0	28	85	85
Johnsongrass	0	15	86	85
Rice	0	0	56	50
Sorghum	0	46	76	73
25 Wheat	0	0	46	26
Field corn	0	13	63	63
MEAN GRASSES	0	21	80	75
Sugarbeets	0	0	0	0
Canola	1	0	3	1
30 Soybean	1	3	1	3
Cotton	6	0	0	0
MEAN BROADLEAF CR	2	1	1	1

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Conclusion: Select at 11 gr/ha without the adjuvant has poor activity on grasses. The activity of Select is increased significantly by adding 0.125 or 0.25% (v/v.) adjuvant to the spray solution.

TABLE 3

Effect of Different Additives on the
Percent Phytotoxicity of Select
Greenhouse Test

5	Weeds and Crop Plants	SELECT	SELECT	SELECT	SELECT	SELECT
		0 gr/ha ADJUVANT 1% v/v	5 gr/ha ADJUVANT 0% v/v	5 gr/ha ADJUVANT 0.3% v/v	5 gr/ha AGRIDEX ** 0.3% v/v	0gr/ha AGRIDEX 1% v/v
10	Blackgrass	0	10	55	20	0
	Crabgrass	0	10	90	30	0
	Goosegrass	0	25	65	45	0
	Sprangletop	0	10	90	30	0
	Italian Ryegrass	0	30	90	75	0
15	Proso millet	0	80	94	90	0
	Wheat	0	0	40	15	0
	Barley	0	0	60	0	0
	MEAN GRASSES	0	21	73	38	0

**Agridex is a commercial adjuvant containing 80% (wt)
paraffinic oil and approximately 20% (wt) nonionic surfactant.

20 Conclusions:

1. Adjuvant is not phytotoxic even at 1%.
2. Adjuvant at 0.3% v/v in the spray solution is more effective than Agridex and dramatically enhances the activity of Select.

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TABLE 4

Effect of Different Additives on the
Percent Phytotoxicity of Select
Greenhouse Test

5

Weeds and Crop Plants	SELECT 0 gr/ha ADJUVANT 1% v/v	SELECT 5 gr/ha ADJUVANT 0% v/v	SELECT 5 gr/ha ADJUVANT 1% v/v	SELECT 5 gr/ha AGRIDEX 1% v/v	SELECT 0 gr/ha AGRIDEX 1% v/v
Blackgrass	0	10	80	70	0
Crabgrass	0	10	90	70	0
10 Goosegrass	0	25	70	55	0
Sprangletop	0	10	90	40	0
Italian Ryegrass	0	30	90	75	0
Proso millet	0	80	95	80	0
15 Wheat	0	0	50	15	0
Barley	0	0	60	0	0
MEAN GRASSES	0	21	78	51	0

Conclusions:

- 20 5 gr/ha Select and 1% adjuvant resulted in 80% or higher control of five out of eight grassy species. The same rate of Agridex plus SELECT gave 80% control of one out of eight grassy species.

TABLE 5

Effect of Different Additives on the
Percent Phytotoxicity of Select
Greenhouse Test

5	Weeds and Crop Plants	SELECT 0 gr/ha ADJUVANT 1% v/v	SELECT 11 gr/ha ADJUVANT 0% v/v	SELECT 11 gr/ha ADJUVANT 0.3% v/v	SELECT 11 gr/ha AGRIDEX 0.3% v/v	SELECT 0 gr/ha AGRIDEX 1% v/v
10	Blackgrass	0	60	80	70	0
	Crabgrass	0	65	95	80	0
	Goosegrass	0	65	90	92	0
	Sprangletop	0	57	98	50	0
	Italian Ryegrass	0	70	95	98	0
15	Proso millet	0	90	100	95	0
	Wheat	0	25	75	40	0
	Barley	0	0	85	0	0
	MEAN GRASSES	0	54	90	66	0

Conclusions:

20 11 gr/ha Select plus 0.3% v/v Adjuvant gave 80% or higher control of seven out of eight grass species. Agridex at the same rate gave 80% or higher control of four out of eight grassy species.

TABLE 6

Effect of Different Additives on the
Phytotoxicity of Select Under Field Conditions

	Herbi- cide rate g/ha	Additive rate % v/v	Johnson- grass	Grain Sorghum	Broadleaf Signal- grass	Grain Fox- tail	Barnyard Grass
5	Select 20	Adjuvant 0	1.00	0.67	0	0.0	0.0
10	Select 20	Adjuvant 0.5	5.67	7.67	6.83	5.00	7.33
	Select 20	Agridex 0.5	1.00	1.33	0.0	0.0	0.33
15	Select 20	Dash 0.5	1.67	1.33	2.00	0.67	1.67
	Select 40	Adjuvant 0	3.67	3.67	3.33	3.0	3.3
20	Select 40	Adjuvant 0.5	8.00	10.00	10.00	7.3	9.33
	Select 40	Agridex 0.5	5.00	5.33	8.36	4.91	6.02
	Select 40	Dash 0.5	8.17	7.00	8.00	6.0	8.17
25	Observation made 4 weeks after treatment using scale of 0-10, where 10 is complete kill of plant. 280 l/ha. spray. Field test: Fresno, CA						
	Dash is an adjuvant similar to those disclosed in European Patent Application 0356 812-A2.						
30	Growth Stages at Treatment:						
	Johnson Grass	-	6-8" tall				
	Grain Sorghum	-	8" tall				
	Broadleaf Signalgrass	-	1-2" tall				
35	Green Foxtail	-	6-7" tall				
	Barnyard Grass	-	5-6" tall				
Conclusion: The overall performance of Select +0.5% adjuvant was better than Select plus 0.5% of Agridex or Dash.							

WHAT IS CLAIMED IS:

1. A method of enhancing uptake and transport of a plant-active agent into a living plant, said agent being capable of effecting a physiological response within said plant and said agent having a molecular structure capable of equilibrating to acidic and basic species in the presence of water; comprising the step of contacting said plant with an amount of said agent effective to obtain said physiological response in said plant in the presence of a non-phytotoxic uptake-enhancing amount of an uptake-enhancing adjuvant, said adjuvant comprising

(a) 20-60% (w/w) of an anionic surfactant of the formula:

15



wherein X is HO- or $\text{-(O(CH}_2\text{)}_m\text{)}_n\text{OR}'$; X' is $\text{-(O(CH}_2\text{)}_m\text{)}_n\text{OR}'$;
 20 R' is an alkyl or alkaryl group containing 5-50 carbon atoms;

m is 2 to 3; and

n is an integer from 1 to about 50;

R⁵ is linear or branched alkyl or alkenyl containing
 25 6 to about 50 carbon atoms, or R⁵ is

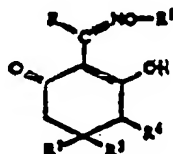


wherein R⁶ is alkyl or alkenyl containing 1 to about 30 carbon atoms;

(b) 40-60% (w/w) of fatty acids, fatty acid esters or mixtures thereof; and

30 (c) 10-40% (w/w) of polyalkylene glycol esters of fatty acids.

2. A method according to Claim 1 wherein said plant-active agent is a herbicide, fungicide, insecticide, plant growth regulator or a mixture thereof.
3. A method according to Claim 2 wherein said
5 surfactant has a pKa in the range of 0.1 to 5.
4. A method according to Claim 2 wherein said plant active agent is a herbicide.
5. A method according to Claim 4 wherein said herbicide is of the formula:



- 10 wherein
- R is alkyl of 1 to 6 carbon atoms or phenyl;
- R¹ is haloalkenyl of 2 to 6 carbon atoms and 1 to 3 halogen atoms, p-halobenzyl or p-trifluoromethylbenzyl;
- R² and R³ are independently hydrogen, alkyl of 1 to 3
15 carbon atoms, alkylthio of 1 to 6 carbon atoms, or alkylthioalkyl of 2 to 8 carbon atoms;
- R⁴ is hydrogen or carbalkoxy of 2 to 4 carbon atoms.
6. The method of Claim 5 wherein R⁴ is hydrogen.
7. The method of Claim 6 wherein R is alkyl of 1 to
20 6 carbon atoms.
8. The method of Claim 7 wherein R¹ is said haloalkenyl.
9. The method of Claim 8 wherein one of R² and R³ is hydrogen and the other is alkylthioalkyl.

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10. The method of Claim 9 wherein R is ethyl or propyl and one of R² or R³ is hydrogen and the other is 2-ethylthiopropyl.
11. The method of Claim 10 wherein R' is 3-trans-
5 chloroallyl.
12. A method according to Claim 1 wherein X is -OH.
13. A method according to Claim 1 wherein X is $\text{-(O(CH}_2\text{)}_m\text{)}_n\text{OR}$.
14. A method according to Claim 1 wherein said
10 surfactant comprises a mixture of compounds wherein X=-OH and $\text{X=-(O(CH}_2\text{)}_m\text{)}_n\text{OR}$.
15. A method according to Claim 14 wherein m=2.
16. A method according to Claim 15 wherein R' is dialkylphenyl.
- 15 17. A method according to Claim 16 wherein R' is dinonylphenyl.
18. A method according to Claim 15 wherein n=3.
19. A method according to Claim 18 wherein R' is alkyl.
20. A method according to Claim 19 wherein R' is
20 tridecyl.
21. A method according to Claim 1 wherein said adjuvant comprises a combined 70% by weight of the components (b) and (c).

22. A method according to Claim 1 wherein the components in (b), and (c) are selected from the group consisting of vegetable-derived oils, and mixtures thereof.

23. A method according to Claim 22 wherein said components have vapor pressures less than about 3 mm of Hg at 20°C.

24. A plant-active composition comprising a plant-active agent, said agent being capable of effecting a physiological response within said plant and said agent having a molecular structure capable of equilibrating to acidic and basic species in the presence of water comprising an amount of said agent effective to obtain said physiological response in said plant, and a non-phytotoxic uptake-enhancing amount of an uptake-enhancing adjuvant, said adjuvant comprising

(a) 20-60% (w/w) of an anionic surfactant of the formula:



wherein X is HO- or $\text{-(O(CH}_2\text{)}_m\text{)}_n\text{OR}'$; X' is $\text{-(O(CH}_2\text{)}_m\text{)}_n\text{OR}'$;

R' is an alkyl or alkaryl group containing 5-50 carbon atoms;

m is 2 to 3; and

n is an integer from 1 to about 50;

R⁵ is linear or branched alkyl or alkenyl containing 6 to about 50 carbon atoms, or R⁵ is



30 wherein R⁶ is alkyl or alkenyl containing 1 to about 30 carbon atoms;

(b) 40-60% (w/w) of fatty acids, fatty acid esters or mixtures thereof; and

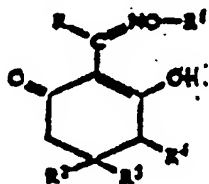
(c) 10-40% (w/w) of polyalkylene glycol esters of fatty acids.

25. A composition according to Claim 24 wherein said plant-active agent is a herbicide, fungicide,
5 insecticide, plant growth regulator or a mixture thereof.

26. A composition according to Claim 25 wherein said surfactant has a pKa in the range of 0.1 to 5.

27. A composition according to Claim 25 wherein said plant active agent is a herbicide.

10 28. A composition according to Claim 27 wherein said herbicide is of the formula:



wherein

R is alkyl of 1 to 6 carbon atoms or phenyl;

R¹ is haloalkenyl of 2 to 6 carbon atoms and 1 to 3

15 halogen atoms, p-halobenzyl or p-trifluoromethylbenzyl;

R² and R³ are independently hydrogen, alkyl of 1 to 3 carbon atoms, alkylthio of 1 to 6 carbon atoms, or alkylthioalkyl of 2 to 8 carbon atoms;

R⁴ is hydrogen or carbalkoxy of 2 to 4 carbon atoms.

20 29. The composition of Claim 28 wherein R⁴ is hydrogen.

30. The composition of Claim 29 wherein R is alkyl of 1 to 6 carbon atoms.

31. The composition of Claim 30 wherein R¹ is said haloalkenyl.

32. The composition of Claim 31 wherein one of R^2 and R^3 is hydrogen and the other is alkylthioalkyl.
33. The composition of Claim 32 wherein R is ethyl or propyl and one of R^2 or R^3 is hydrogen and the other is
5 2-ethylthiopropyl.
34. The composition of Claim 33 wherein R^1 is 3-trans-chloroallyl.
35. A composition according to Claim 24 wherein X is -OH.
- 10 36. A composition according to Claim 24 wherein X is $\text{-(O(CH}_2\text{)}_m\text{)}_n\text{OR}$.
37. A composition according to Claim 24 wherein said surfactant comprises a mixture of compounds wherein $X=-\text{OH}$ and $X=\text{-(O(CH}_2\text{)}_m\text{)}_n\text{OR}$.
- 15 38. A composition according to Claim 37 wherein $m=2$.
39. A composition according to Claim 15 wherein R' is dialkylphenyl.
40. A composition according to Claim 39 wherein R' is dinonylphenyl.
- 20 41. A composition according to Claim 38 wherein $n=3$.
42. A composition according to Claim 41 wherein R' is alkyl.
43. A composition according to Claim 42 wherein R' is tridecyl.

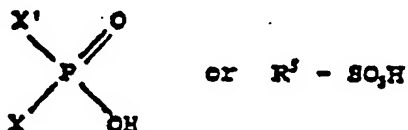
44. A composition according to Claim 24 wherein said adjuvant comprises a combined 70% by weight of the components (b) and (c) and 30% of said anionic surfactant.

5 45. A composition according to Claim 24 wherein the components in (b) and (c) are selected from the group consisting of vegetable-derived oils, and mixtures thereof.

46. A composition according to Claim 45 wherein said
10 components have vapor pressures less than about 3 mm of Hg at 20°C.

47. An adjuvant composition for enhancing the uptake and transport of a plant-active agent comprising

(a) 20-60% (w/w) of an anionic surfactant of the
15 formula



wherein X is HO- or $\text{O}(\text{CH}_2)_m\text{OR}'$; X' is $\text{O}(\text{CH}_2)_m\text{OR}'$;
R' is an alkyl or alkaryl group containing 5-50
carbon atoms;

m is 2 to 3; and

20 n is an integer from 1 to about 50;

R⁵ is linear or branched alkyl or alkenyl containing
6 to about 50 carbon atoms, R⁵ is



wherein R⁶ is alkyl or alkenyl containing 1 to about 30
carbon atoms;

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(b) 40-60% (w/w) of fatty acids, fatty acid esters or mixtures thereof; and

(c) 10-40% (w/w) of polyalkylene glycol esters of fatty acids.

5 48. A composition according to Claim 47 wherein X is -OH.

49. A composition according to Claim 47 wherein X is $\text{-(O-(CH}_2\text{))}_m\text{-OR}$.

50. A composition according to Claim 47 wherein said surfactant comprises a mixture of compounds wherein X
10 = -OH and $\text{X=-(O-(CH}_2\text{))}_m\text{-OR}$.

51. A composition according to Claim 50 wherein m = 2.

52. A composition according to Claim 51 wherein R' is dialkylphenyl.

53. A composition according to Claim 52 wherein R' is
15 dinonylphenyl.

54. A composition according to Claim 51 wherein n = 3.

55. A composition according to Claim 54 wherein R' is alkyl.

56. A composition according to Claim 55 wherein R' is
20 tridecyl.

57. A composition according to Claim 47 wherein said adjuvant comprises a combined 70% by weight of the components (b) and (c) and 30% of said anionic surfactant.

58. A composition according to Claim 47 wherein the components in (b) and (c) are selected from the group consisting of vegetable-derived oils, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 90/05973

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC(5) A01N 25/24, 25/30, 31/04, 33/02, 37/00, 61/00 U.S. Cl. 71/65
 B01F 17/00, 17/06, 17/14, 17/20

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System ¹

Classification Symbols

US 71/65, 98, 106, 121, Dig. 1
 252/351
 514/1

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁴
Y	JP, A 55-89203 (NIPPON SODA KK) 5 July 1980 (05.07.80)	1-58
Y	US, A 4,380,661 (SUCHY), 19 Apr 1983, see column 6; lines 1-28.	1, 2, 12-20, 25 35-43, 47-56
Y	US, A 4,436,547 (SAMPSON), 13 Mar 1984	1-58
Y	US, A 4,497,804 (KUDAMATSU ET AL), 5 Feb 1985, see columns 5-6.	1, 2, 12-20, 25 35-43, 47-56
Y	US, A 4,504,305 (IWATAKI ET AL), 12 Mar 1985	1-58
Y	US, A 4,609,669 (KUME ET AL), 2 Sept 1986, see columns 8-9.	1, 2, 12-20, 25 35-43, 47-56
Y	US, A 4,640,708 (BIRD ET AL), 3 Feb 1987	1-58

¹⁶ Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹

17 January 1991

International Searching Authority ¹

ISA/US

Date of Mailing of this International Search Report ¹

26 FEB 1991

Signature of Authorized Officer ¹⁰

S. MARK CLARDY

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

See form PCT/ISA/206

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, ^{1a} with indication, where appropriate, of the relevant passages ^{1b}	Relevant to Claim No. ^{1c}
Y	US, A 4,666,510 (WATSON ET AL) 19 May 1987	1-58
Y	US, A 4,710,518 (KURAHASHI ET AL), 1 Dec 1987, see columns 8-9	1, 2, 12-20-25, 35-43, 47-56
Y	US, A 4,780,129 (BECKER ET AL), 25 Oct 1988	1-58
Y	US, A 4,797,152 (BRUNNER), 10 Jan 1989	1-58
X	US, A 4,834,908 (HAZEN ET AL), 30 May 1989	1-58
A	US, A, 4,886,545 (PECK ET AL), 12 Dec 1989	
E	US, A 4,966,621 (HEINRICH ET AL), 30 Oct 1990 see column 3-5	1, 2, 12-20,25, 35-43, 47-56
E	US, A 4,966,728 (HAZEN), 30 Oct. 1990	1-58